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HIGH TEMPERATURE MEASUREMENTS OF THE RATE OF UPTAKE OF TeO_2 VAPOR BY SELECTED OXIDES

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ABSTRACT

In a program for elucidation of the process of formation of radioactive fallout, we measured the rates at which substrate samples of calcium ferrite and of clay loam took up vaporized TeO_2. The rate measurements were made for uptake in air from 900 to 1500°C and over a TeO_2 partial-pressure range of about 5×10^{-7} to 2×10^{-4} atm. We found that the rate of uptake of TeO_2 by the calcium ferrite was two to three orders of magnitude faster than the rate of uptake by the clay loam. The rate-controlling process for the uptake of TeO_2 vapor by the calcium ferrite was the diffusion of the TeO_2 vapor molecules through the air. No unique rate-controlling process was found for the uptake of TeO_2 vapor by the clay loam. In this system, the rate seemed to be controlled both by a slow rate of reaction of the TeO_2 at the clay loam surface and by the slow diffusion of the condensed TeO_2 into the clay loam.

SUMMARY

The Problem

Much effort has been put into developing mathematical models of the radioactive-fallout formation process for the purpose of predicting the radiation exposure rates and exposures in the fallout fields resulting from nuclear explosions. One of the most important parameters in such models is the rate at which vaporized radioactive elements or compounds are taken up by molten and solid particles at high temperatures. Essentially no measurements have been made of these rates. It is the purpose of this investigation to measure some of these uptake rates for TeO_2, and, if possible, to discover the rate-controlling steps in the high-temperature uptake process.

The materials used in the investigation were among those found in radioactive fallout. $^{127m}TeO_2$ was chosen as the radioactive vapor and the substrate materials were a clay loam (typical of fallout material derived from a silicate soil) and a calcium ferrite (similar to the composition of some types of fallout particles from the Pacific Proving Grounds).

Findings

Most of the measurements of the rate of uptake of the TeO_2 vapor onto spherical particles of the substrate samples fall into three categories. The first group consists of measurements made at constant temperatures (1400°, 1200° and 1000°C) and constant TeO_2 partial pressure (about 10^{-5} atm) but with varying sample particle diameters (about 0.16 to 0.40 cm). The results are shown graphically in terms of uptake of TeO_2 per particle in μg/min. It was found that the rate of uptake

by the calcium ferrite was about two to three orders of magnitude faster than the rate of uptake by the clay loam.

The second group of measurements was made with constant particle diameter (0.3 cm) and constant temperature (1400°C) but with varying TeO_2 pressure (5×10^{-7} to 2×10^{-4} atm). The third group of measurements was made with constant particle diameter (0.3 cm) and constant TeO_2 pressure ($9.2 \quad 10^{-6}$ atm) but with varying temperature (900 to 1500°C). These results are also presented graphically in the same terms as above.

For interpretation of the data, it was postulated that the uptake process consisted of three steps: (1) the diffusion of the TeO_2 vapor through the air to the surface of the substrate particle, (2) the reaction or condensation of the TeO_2 vapor onto the surface of the particle, and (3) the diffusion of the condensed TeO_2 from the surface of the particle into the interior.

For the uptake of TeO_2 vapor onto the calcium ferrite, it was found that the diffusion of the TeO_2 through the air was the rate-controlling step. By use of Maxwell's equation, it was possible to make theoretical predictions of the rate of uptake of the TeO_2 onto the calcium ferrite; these predictions agreed moderately well with the experimentally measured values.

For TeO_2 uptake onto the clay loam particles, no unique rate-controlling step was found; rather the rate seemed to be governed both by the rate of reaction of the TeO_2 at the surface of the particle and by the diffusion of the TeO_2 into the particle. With the limited kinetic data obtained, no method of making theoretical extrapolations of the uptake rate was discovered for the clay loam, but empirical extrapolations of the data are, of course, possible.

CONTENTS

INTRODUCTION

This is the second in a series of reports describing experimental studies of the rates of uptake of selected vaporized oxides by molten oxide substrates at high temperatures. The purposes of these studies are to provide data which can be used in radioactive-fallout prediction models and to discover the mechanisms which govern the rates of uptake of the vaporized oxides. Volatile radioactive oxides of elements from important fission-product mass chains are used as the vapor sources, and inert, non-volatile oxides of materials that form radioactive fallout particles are used as the molten substrates.

The first report of this series presented the results of measurements of the uptake rate of MoO_3 vapor by molten substrates of calcium ferrite and of a clay loam soil occurring in the Berkeley Hills, California.[1] The clay loam soil was more or less typical of silicate soils found in extensive areas in the temperate zones. The calcium ferrite has been observed in fallout resulting from nuclear explosions at the Pacific Proving Grounds where large amounts of calcium oxide, derived from the coral sand, and iron oxide, derived from the towers, barges and other structures, have been fused together. This report presents the results of measurements of the uptake rate of TeO_2 vapor upon these same two substrate materials. TeO_2 was chosen as the radioactive vapor because it is one of the important volatile radioactive constituents of fallout and is the precursor of the volatile radioelement iodine. Radioiodine, particularly ^{131}I, ^{132}I, ^{134}I and ^{135}I, makes large contributions to both the external and the internal hazard from fallout.

EXPERIMENTAL METHOD

Description of Apparatus

Whereas the experimental apparatus and method have been described in detail in the first report of this series, only a brief summary will be given here. The apparatus consisted mainly of a vertical tube furnace 74 cm long and 2.2 cm I.D. (Fig. 1). The furnace tube was made of dense, gas-tight, high purity alumina (McDanel Refractory Porcelain Co., Beaver Falls, Pa.). Two independent heating circuits were wound on the exterior of the tube. The top, high temperature, circuit was wound with 17-gauge Pt-20 % Rh wire and the bottom, low temperature, circuit was wound with 17-gauge Kanthal A-1 wire.

The radioactive TeO_2, which served as the vapor source, was contained in a small platinum crucible which was positioned in the low temperature zone of the furnace on top of an assembly of two porous alumina plugs which were mounted on a small gas-tight alumina tube. The substrate samples were pre-fused, nearly spherical beads formed on platinum wire loops. The platinum loops holding the samples were suspended in the high-temperature zone of the furnace. Temperature measurements were made with two Pt-10 % Rh thermocouples; one was placed next to the vapor source in the low-temperature zone and the other was placed next to the suspended substrate sample in the high-temperature zone. The radioactive TeO_2 vapor was carried from the low temperature zone up into the high-temperature zone by a steady flow of dry air which was introduced into the furnace through a hole in the small, gas-tight alumina tube which supported the vapor source. The interior of the alumina furnace tube was protected from the TeO_2 vapor by a platinum-foil liner. Three perforated platinum-foil diaphragms were placed at intervals between the vapor source and the high-temperature zone in order to protect the vapor source from direct

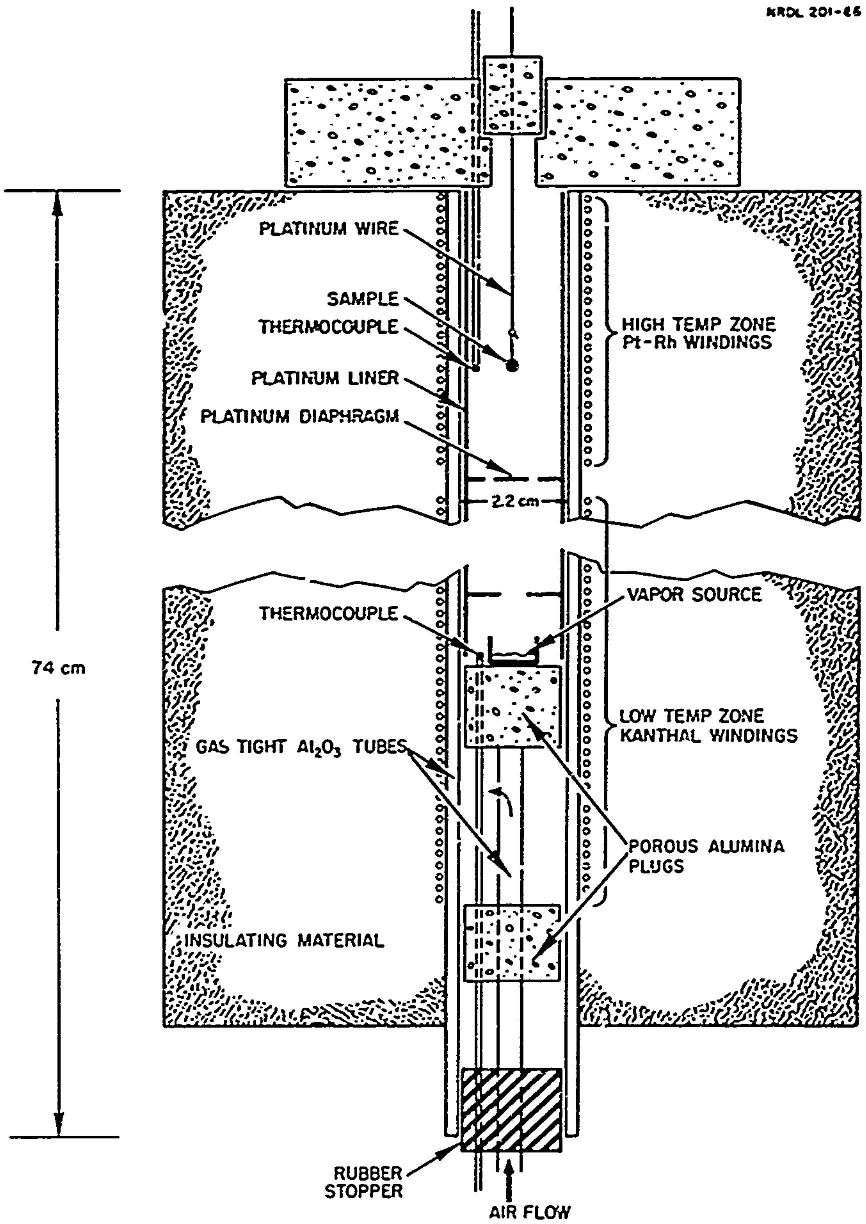

Fig. 1 Two-Temperature Furnace

radiation from the high-temperature zone, and to insure mixing of the TeO_2 vapor with the carrier gas.

Preparation of Materials and Samples

The TeO_2 vapor source was prepared as follows: Na_2TeO_4 was placed in concentrated HCl, where it formed a slurry. To this slurry was added radioactive tellurium (^{127m}Te) in the form of H_2TeO_3 in HCl solution (as supplied by New England Nuclear Corp., Boston, Mass.).* Boiling of the Na_2TeO_4-$^{127m}TeO_3$ slurry in HCl solution reduced the tellurium and this brought about solubility of the carrier salt and completion of exchange with tellurium tracer. Boiling reduces Na_2TeO_4 to tellurous acid (H_2TeO_3) and causes release of chlorine gas. The solution was boiled down to a small volume, more concentrated HCl was added and the solution was boiled down again for insurance of complete reduction and carrier-tracer exchange. Concentrated HNO_3 was then added and the solution again evaporated to a small volume for removal of the remaining HCl and the oxidation of some of the exchanged carrier salt. The HNO_3 boildown was repeated once more. Water was then added, followed by enough concentrated NH_4OH (only a few drops) to just neutralize the solution and precipitate H_2TeO_4. The solution and precipitate were placed in a hot water bath and oxygen was vigorously bubbled through for 10 to 15 minutes for completion of oxidation. The salt at this point was converted predominantly to H_2TeO_4. Concurrently with the addition of oxygen, a drop or two of concentrated NH_4OH was carefully added until precipitation was complete.

The solution and precipitate were transferred to a conical centrifuge tube, centrifuged, the supernate decanted, the precipitate washed with freshly oxygenated dilute NH_4OH and then recentrifuged. The

*For a check of the radiological purity of the tellurium, its decay was followed for about two months and its half life was found to be 105 days, which corresponds exactly to the published half life of ^{127m}Te.

washing procedure was repeated once with additional dilute NH_4OH and then 3 times with acetone. The washed precipitate was dried on a hot water bath. For prevention of caking the precipitate was rapidly stirred with a platinum wire while drying. The dry powdered precipitate was then heated in a furnace at 500°C for about 24 hours in order to convert all the acidic and hydrated oxide forms of tellurium to TeO_2. The final composition was checked by X-ray diffraction powder analysis.

The calcium ferrite used for the substrate samples was prepared by weighing out the appropriate amounts of AR grade Fe_2O_3 and CaO powders so that the final composition of the mixture would be 80 % Fe_2O_3 and 20 % CaO by weight. The dry powders were mixed thoroughly in a mortar. The powders were fused directly on the platinum wire loops in the flame of a gas-oxygen torch.

The clay loam was prepared by first being sieved to remove the larger pebbles and pieces of organic matter. The material passing the sieve was dried and ground and then melted in a nickel crucible at about 1300-1400°C for about an hour. Upon cooling, the melt formed a black glass which was broken up and ground to a powder in a steel mortar. An analysis of the soil for the non-volatile oxides was made by Metallurgical Laboratories, Inc., San Francisco, Calif. These oxides comprise 89 % of the original clay loam; the remaining 11 % are volatile oxides and minor constituents. The results obtained are as follows:

Oxide	Weight. %
SiO_2	67.5
Al_2O_3	15.9
Fe_2O_3	7.3
CaO	2.7
MgO	2.7
Na_2O	2.3
K_2O	1.6
	100.0

Experimental Procedure

In preparation for a series of experimental runs, the top and bottom sections of the furnace were brought to their proper operating temperatures, the air flow was started, and a standby source of TeO_2 was inserted into the lower section of the furnace. The furnace was allowed to equilibrate with the TeO_2 vapor under the chosen operating conditions for 24 hours prior to each experimental run. About 3 hours before the start of each experimental run, another TeO_2 source, which had just been weighed, was substituted for the standby source in the lower part of the furnace.

During the actual experimental runs, the substrate samples were preheated in a gas flame and then inserted into the top of the furnace for varying lengths of time, usually 2 to 20 minutes depending upon the rate of uptake of TeO_2. At the end of this interval, the samples were quickly withdrawn and were counted in a 3 x 3 in. thallium-activated NaI well-crystal detector. After being counted, the samples were reinserted into the furnace and the procedure repeated. The total accumulated time in the furnace for each sample was usually about 30 to 60 minutes.

At the end of each day's runs, the TeO_2 source was removed from the furnace and replaced by the standby source. The TeO_2 source was then reweighed for determination of the amount of TeO_2 which had evaporated. The vapor concentration in the furnace was computed from the amount of TeO_2 evaporated and the known volume of air which passed through the apparatus while the TeO_2 source was in the furnace.

The range of temperatures for the lower level source region was 590°-$712^{\circ}C$ with $660^{\circ}C$ being the temperature used for most of the runs. The flow rate of air through the furnace tube was 61 ml per min.

The actual uptake of TeO_2 by the samples was determined by comparison of the radioactive counting rate of the samples with that of a standard containing a known amount of the same TeO_2 as used in the vapor source. Because of the low energy of the ^{127m}Te gamma emission (0.089 mev) there was appreciable self-absorption in the samples. For correcting for this effect, the following procedure was used. First, a counting standard was prepared by solution of a known weight of the TeO_2 source material in a standard volume of HCl (for calcium ferrite) or HF (for clay loam). Addition of small, weighed quantities of substrate, followed by recounting, served to determine the effect of mass on the counting rate. Next, a series of various-sized samples of both calcium ferrite and clay loam were exposed to TeO_2 vapors for varying times in the furnace. These samples were counted as they were removed from the furnace. The ferrite and clay loam samples were then dissolved in standard volumes of concentrated HCl and HF respectively and recounted. These procedures enabled calibration curves to be drawn which in effect corrected the counting rates of the various sized solid substrate samples to what their counting rates would be when dissolved in the standard volume of liquid (with the appropriate quantity of dissolved substrate material). These corrected counting rates were then compared with the counting rate of the liquid standard for determination of the TeO_2 content of the substrate samples.

Experimental Errors

The precision of the experimentally measured quantities probably exceeds the overall accuracy of the experiment by an order of magnitude. The sample temperatures were known to within about $\pm 4^{\circ}C$ and the weight losses of the TeO_2 vapor source, the volumes of air passed through the furnace, the diameters and weights of the substrate samples, the duration of the time intervals in which the samples were in the furnace and the counting rates of the calcium ferrite and clay loam samples all could be measured to within about ± 5 %. However, the largest uncertainty was in the magnitude of the TeO_2 vapor concentration at the sample position in the furnace. At the low partial pressures of TeO_2 used here, absorption of the TeO_2 on the walls of the furnace could have an important effect. Precautions were taken against this by long periods of equilibration under the operating conditions used in the experimental runs.

A rather crude vapor-sampling technique was used to check the vapor concentration in the furnace. A long, gas-tight alumina tube 0.3 cm I.D., was inserted through a hole in the furnace lid so that the lower end of the tube was near the substrate sample position and the upper end was well above the furnace. A rubber tube was connected to the upper end of the alumina tube and one liter of air together with TeO_2 vapor was slowly withdrawn from the furnace through the alumina tube. As the gas mixture was drawn up, the TeO_2 vapor condensed on the cool inner walls of the tube. The tube was then withdrawn from the furnace and the condensed TeO_2 removed by solution in HCl. The amount of TeO_2 removed was determined radiometrically under the standardized conditions. The recovery was usually about 60-70 % of the predicted recovery based on the calculated vapor concentration in the furnace. These results seem to indicate that the actual TeO_2 vapor concentration in the furnace was 30 to 40 % lower than calculated. However, there is also the possibility of errors in the vapor-sampling technique such as incomplete condensation of the TeO_2 vapor and incomplete removal of the TeO_2 from the tube. It is estimated, when all sources of error are considered, that the data for TeO_2 uptake by the calcium ferrite samples are probably correct to within about a factor of two.

There are two additional sources of error in the measurements with the clay loam particles. First, the uptake of TeO_2 by these particles was so small that the net radioactive counting rates were often less than the 500 cpm background. Second, we observed that the uptake of TeO_2 by the clay loam particles was markedly affected by variations in the heating of the particles during their formation into beads on the platinum wire loops. This was especially true for clay loam samples which were exposed to TeO_2 vapors at temperatures below 1200^{o}. A sample of clay loam which had been heated strongly during its formation was observed to take up TeO_2 at twice the rate of a sample of similar size which had been heated less severely. Because of these uncertainties, we estimate that the absolute accuracy of the rates of uptake of TeO_2 by the clay loam samples is probably no better than a factor of five, although the relative uptake by a series of samples is probably reliable to within a factor of about three.

EXPERIMENTAL DATA

Most of the experimental data can be grouped into three parts: (1) the uptake of TeO_2 as a function of particle size at constant temperature and TeO_2 partial pressure; (2) the uptake of TeO_2 as a function of TeO_2 partial pressure at constant particle size and temperature; and, (3) the uptake of TeO_2 as a function of temperature at constant particle size and TeO_2 partial pressure. The partial pressures of TeO_2 were computed from the vapor concentrations on the assumption that TeO_2 was the vapor species. This assumption was justified by data on the vaporization of fission product oxides[2] which show that, under the conditions of the experiments, TeO_2 is the predominant molecular species in the vapor.

Figures 2, 3 and 4 show the uptake of TeO_2 by various-sized calcium ferrite particles as a function of time at T = 1400, 1200, and $1000^{o}C$ respectively. The TeO_2 partial pressure was held constant for each series of runs. Figures 5, 6 and 7 show the same information for various-sized particles of clay loam.

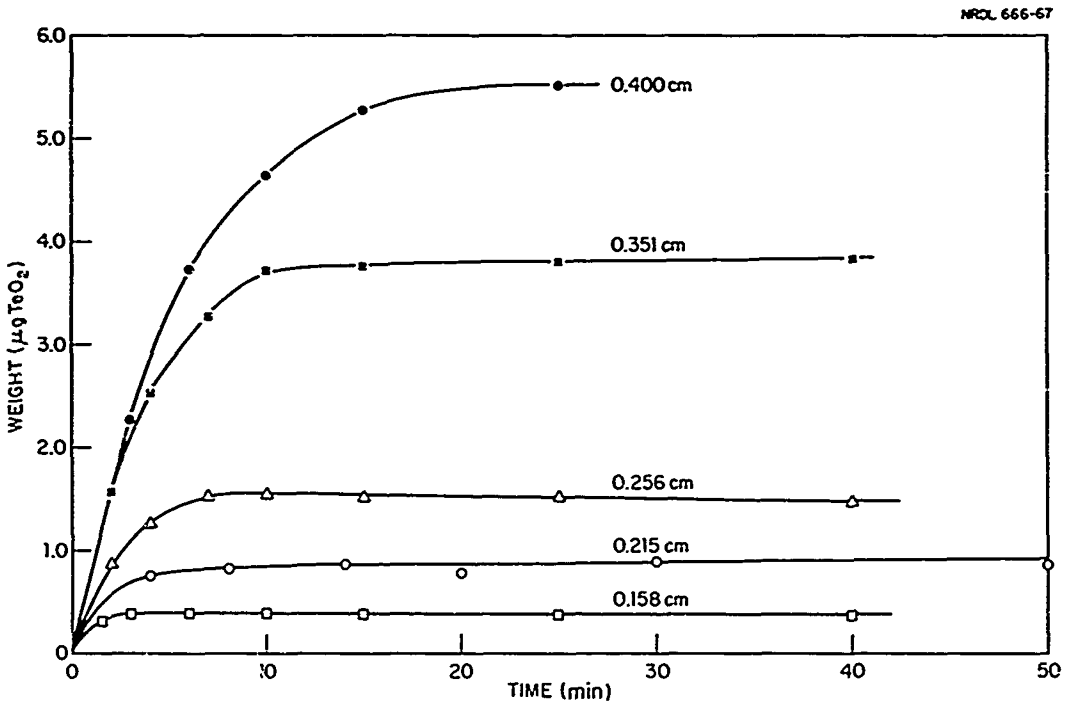

Fig. 2 Uptake of TeO_2 by Calcium Ferrite as a Function of Particle Diameter and Time. T = 1400°C, TeO_2 partial pressure = 9.21×10^{-6} atm.

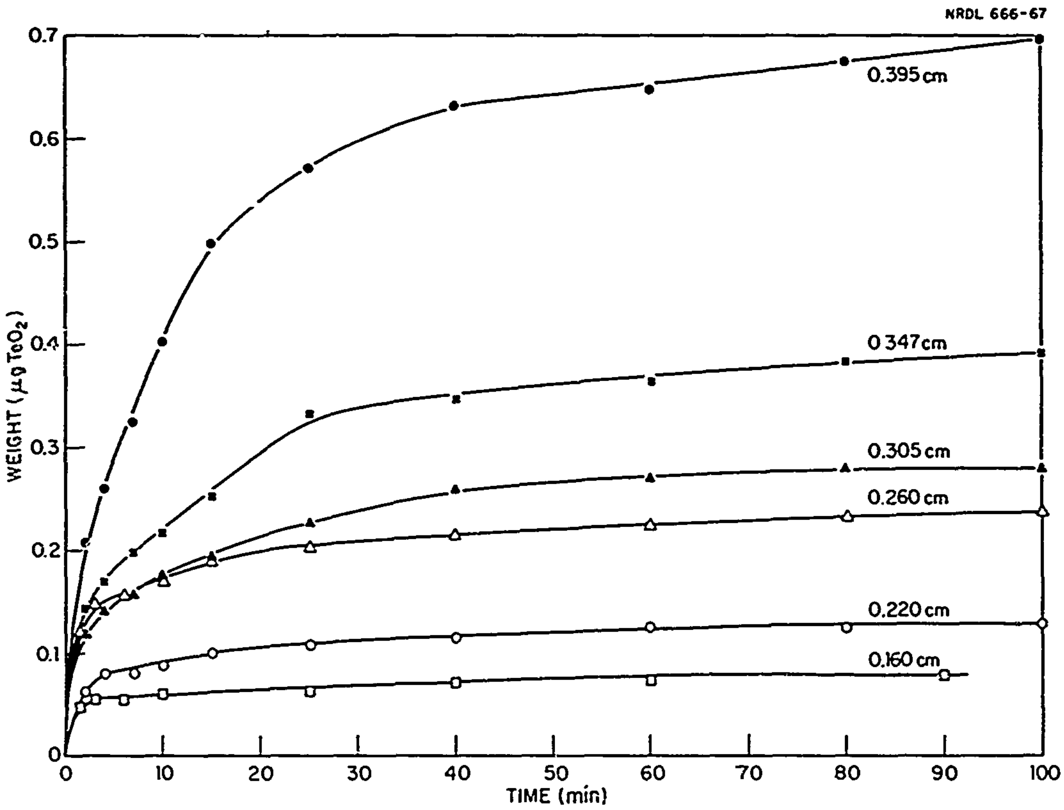

Fig. 3 Uptake of TeO_2 by Calcium Ferrite as a Function of Particle Diameter and Time. $T = 1200^{\circ}C$, TeO_2 partial pressure = 9.21×10^{-6} atm.

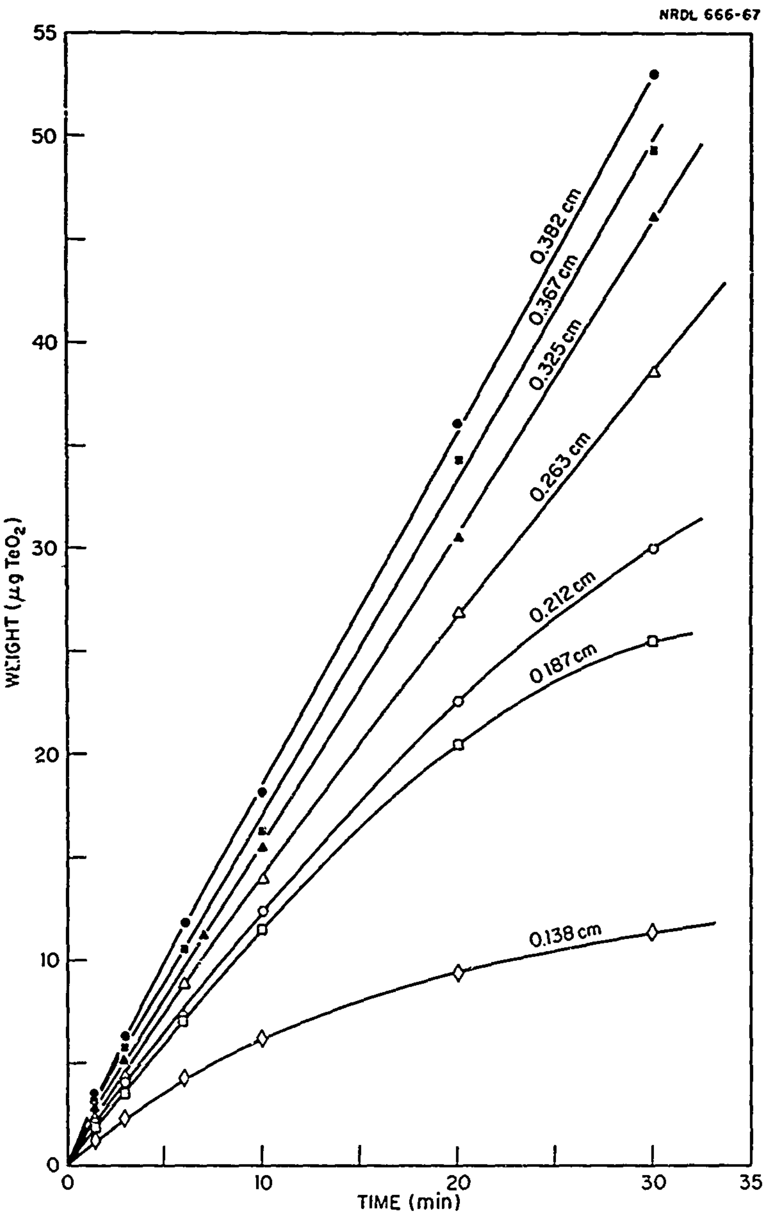

Fig. 4 Uptake of TeO_2 by Calcium Ferrite as a Function of Particle Diameter and Time. T = 1000°C, TeO_2 partial pressure = 1.12×10^{-5} atm.

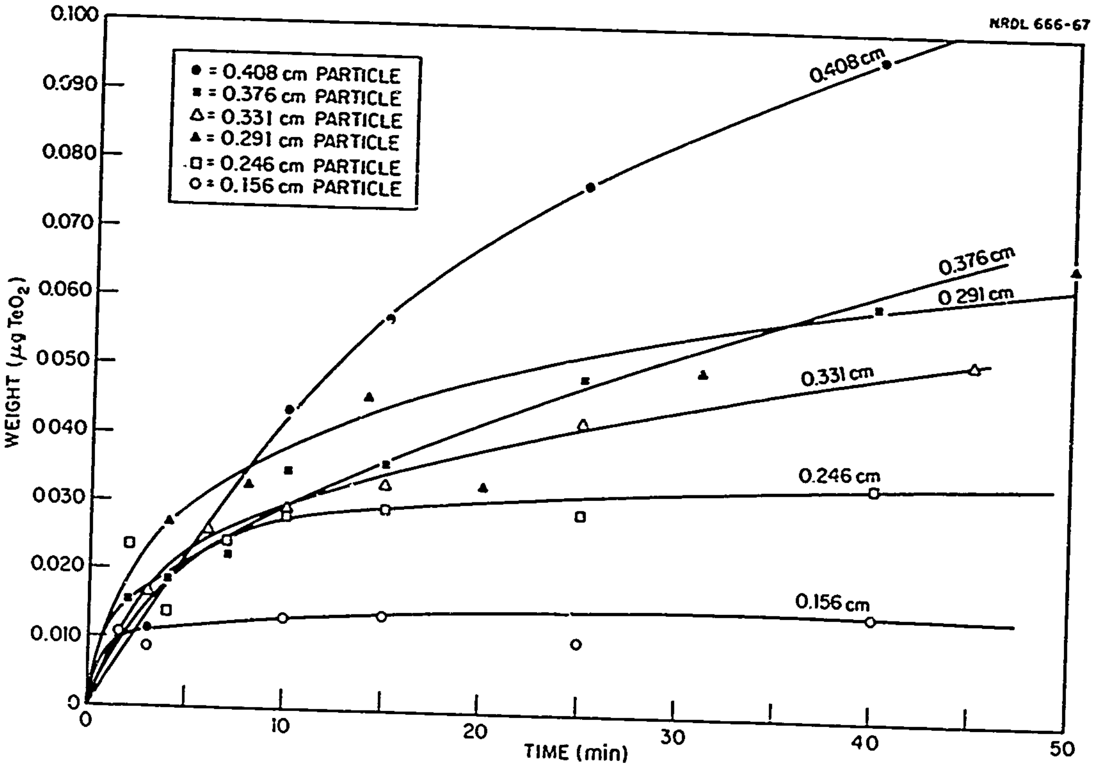

Fig. 5 Uptake of TeO_2 by Clay Loam as a Function of Particle Diameter and Time. $T = 1400°C$, TeO_2 partial pressure = 9.21×10^{-6} atm.

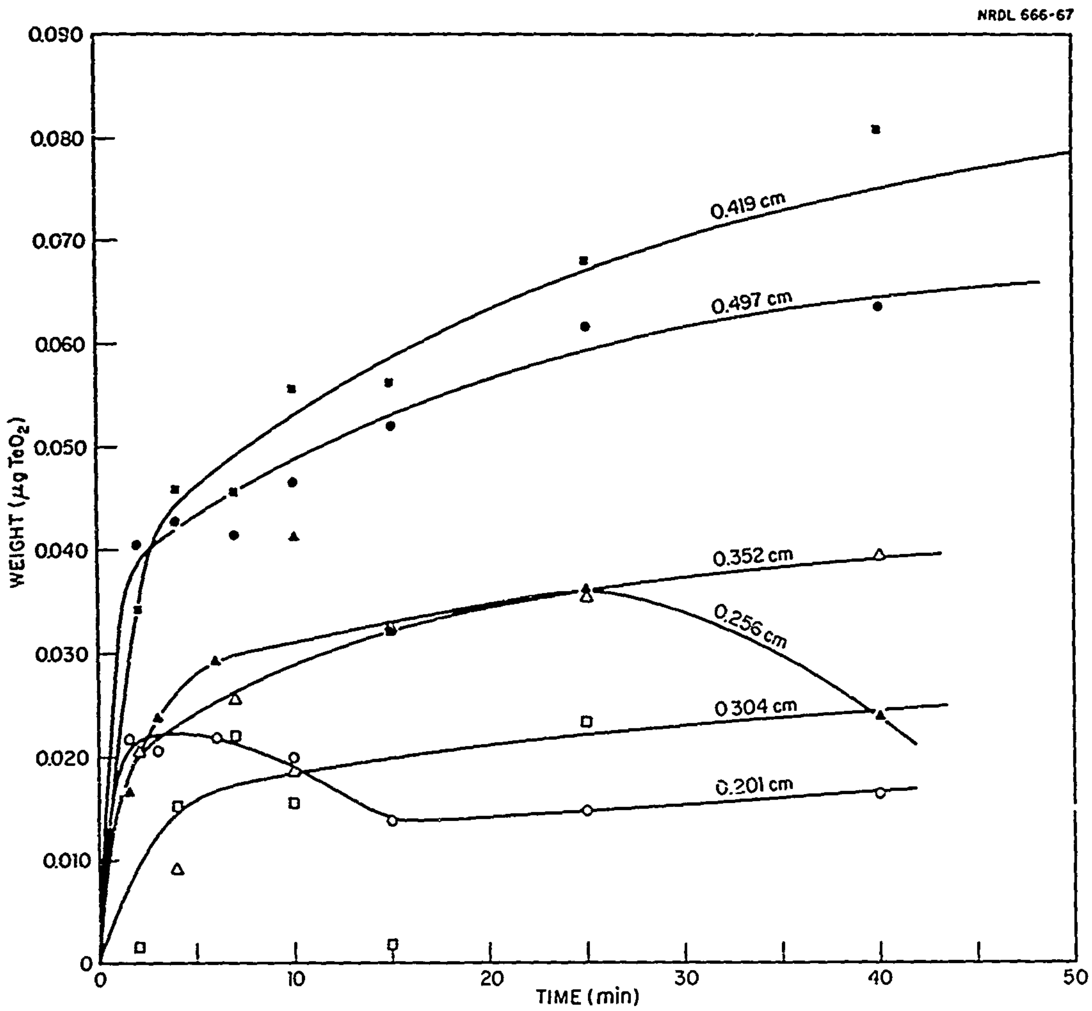

Fig. 6 Uptake of TeO_2 by Clay Loam as a Function of Particle Diameter and Time. $T = 1200^{o}C$, TeO_2 partial pressure = 9.21×10^{-6} atm.

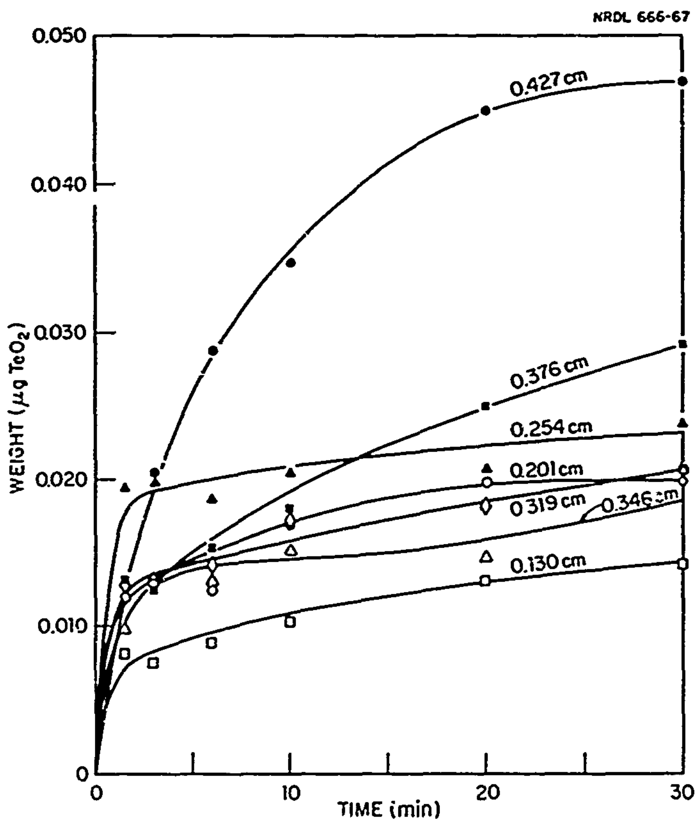

Fig. 7 Uptake of TeO_2 by Clay Loam as a Function of Particle Diameter and Time. T = 1000°C, TeO_2 partial pressure = 1.14×10^{-5} atm.

A large number of runs were made to determine the effects of varying separately the TeO_2 partial pressure and the temperatures of the samples. Within each series of runs the same size particles were used. Figure 8 shows the rates of uptake of TeO_2 by particles 0.302 $\pm$ 0.012 cm in diameter at a temperature of 1400°C and a TeO_2 partial pressure varying from about 5×10^{-7} to 2×10^{-4} atm.

Figures 2 through 7 show that the rates of TeO_2 uptake decrease with time as the particle becomes richer in TeO_2. In Fig. 8 are plotted the initial rates of TeO_2 uptake (that is, the slope of the uptake curve at $t = 0$) by both the calcium ferrite and clay loam samples. The initial rate of uptake has been emphasized because it is independent of the time of exposure of the samples and because it can be used for determination of the mechanism which governs the rate of uptake. Also, it is the rate which would be most applicable to the formation processes of radioactive fallout particles where the total uptake of TeO_2 is too small to change the rate appreciably by saturation effects.

The initial rate of uptake was determined analytically as follows in the case of the calcium ferrite particles which were exposed in the furnace at temperatures above their melting point (1205°C). Figure 2 shows that such calcium ferrite particles reach equilibrium with respect to TeO_2 uptake in a few minutes. By use of the entire uptake curve from $t = 0$ to the equilibrium point, it is possible to solve for the rate constant, k, in the general case of the rate equation,

$$\frac{dx}{dt} = k\ (a-x)^n$$

where x is the TeO_2 uptake at time t, a is the equilibrium uptake and n is the overall order of the uptake reaction with respect to TeO_2 vapor. When k has been determined, n can be found; then at $t = 0$, $x = 0$ and the initial rate is given by:

$$\frac{dx}{dt} = ka^n.$$

For TeO_2 uptake on the calcium ferrite, n was usually close to 1.0. The equilibrium uptake of the TeO_2 by the calcium ferrite particles has also been plotted in Fig. 8.

The analytic method was checked by comparison with the graphically determined slope of the experimental uptake curve at $t = 0$. The initial slopes as determined by the two methods usually agreed to within about 10-20 %. This analytic technique was not used in the determination of the initial rate of TeO_2 uptake, either by the calcium ferrite particles below their melting point or by the clay loam particles, because equilibrium was not reached during the course of such experimental runs. In these cases, the initial rates were determined graphically.

As can be seen in Fig. 5, there is considerable variation possible in drawing the tangents to the uptake curves of the clay loam particles at $t = 0$. This uncertainty has been indicated in Fig. 8 by showing the TeO_2 uptake as vertical lines instead of points. The lengths of the vertical lines indicate the uncertainties in the values of the uptake rates. At $t = 10$ min., there was enough experimental data to establish the uptake curve better. The slopes to the curves at 10 minutes have also been measured, and these rates have been plotted in Fig. 8 for comparison with the initial rates.

Figure 9 shows the effect of temperature changes upon the rates of TeO_2 uptake by the calcium ferrite and clay loam samples. The TeO_2 partial pressure was constant at 9.21×10^{-6} atm. The calcium ferrite particles were 0.297 ± 0.012 cm and the clay loam particles 0.339 ± 0.012 cm in diameter. For determination of the initial rates of TeO_2 uptake by the calcium ferrite particles, the analytical method, checked by the

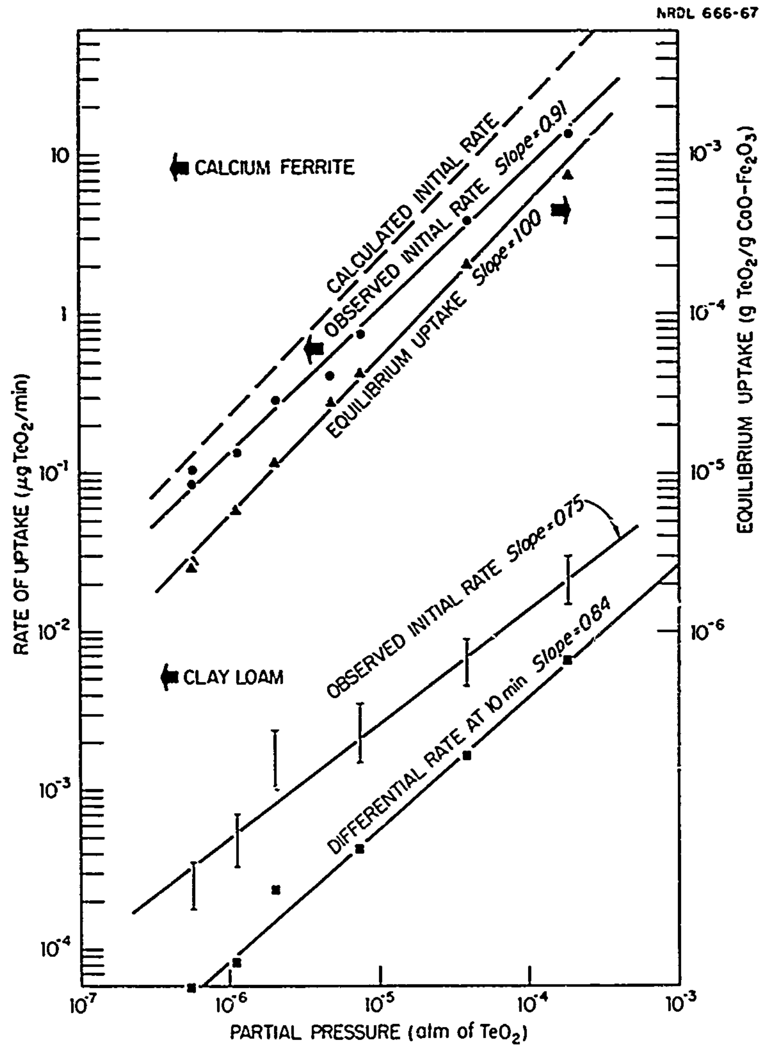

Fig. 8 Rate of Uptake of TeO_2 at 1400°C as a Function of TeO_2 Partial Pressure. The initial rates are shown for both calcium ferrite and clay loam samples. The degree of uncertainty in the rate of uptake by the clay loam samples is indicated by the vertical lines. In addition, the differential uptake rate at 10 minutes is shown for the clay loam samples while the theoretically calculated initial rate (dashed line) and the equilibrium concentration of TeO_2 are shown for the calcium ferrite samples. The average particle diameter is 0.302 ± 0.012 cm.

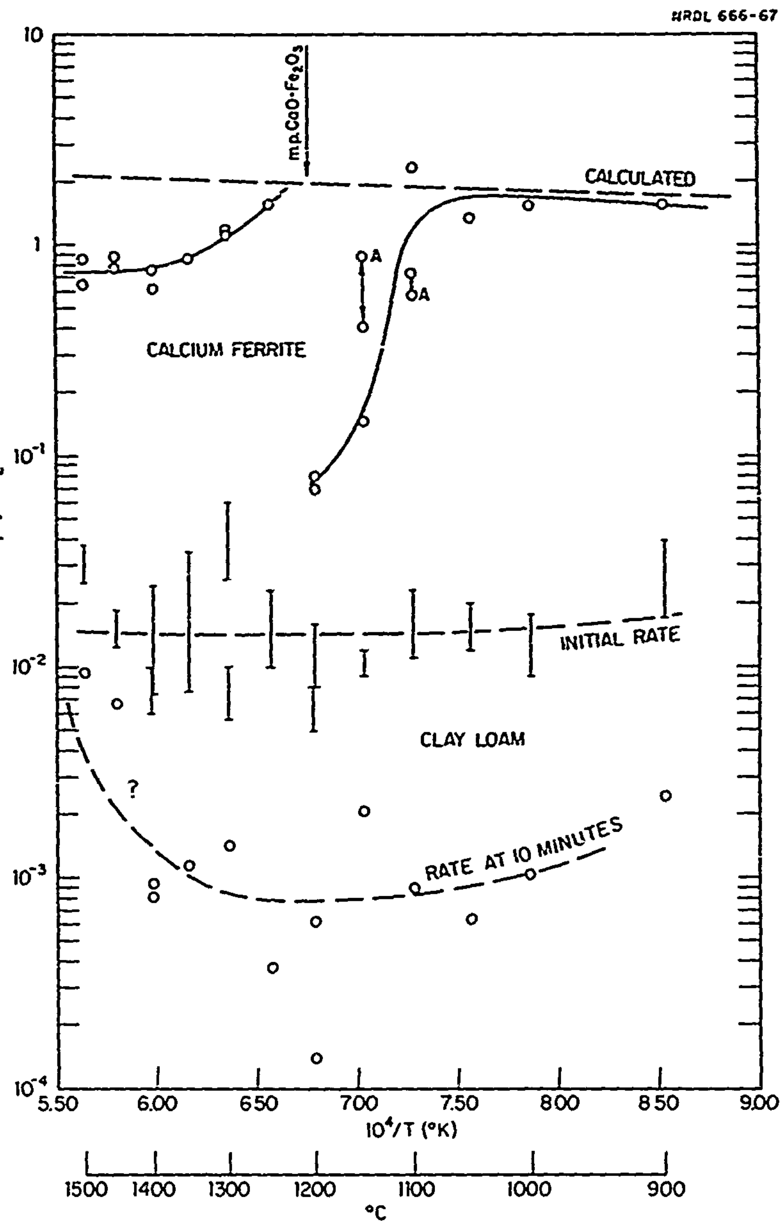

Fig. 9 Rate of Uptake of TeO_2 as a Function of Temperature. The initial rates are shown for both the calcium ferrite and clay loam samples as well as the theoretically calculated rate (upper dashed line) for the calcium ferrite and the uptake rate at 10 minutes for the clay loam samples. "A" refers to the annealed calcium ferrite samples. The TeO_2 partial pressure was 9.21×10^{-6} atm. The average diameter of the calcium ferrite particles was 0.297 ± 0.012 cm and the average diameter of the clay loam particles was 0.339 ± 0.012 cm.

graphical method, was used at temperatures above the calcium ferrite melting point. The graphical method was used at lower temperatures. The methods of measuring and presenting the rate of uptake data for the clay loam particles are the same as for the pressure-variation runs.

A series of runs were made in which the uptakes of TeO_2 by samples of single, unmelted oxides were measured. This was done in order to obtain some information on the relative reactivity of TeO_2 vapor with the various oxides. The furnace temperature was 1400° (below the melting points of all the oxides used) and the TeO_2 partial pressure was 3.46×10^{-5} atm. The samples were prepared by pressing the powdered oxides (AR grade) into thin pellets 0.61 cm in diameter and about 0.05 to 0.08 cm thick. The pellets were backed with platinum foil so that only one face was exposed to the TeO_2 vapor. The uptake of TeO_2 by these oxides is shown in Fig. 10.

DISCUSSION AND INTERPRETATION OF EXPERIMENTAL DATA

Theoretical Introduction

For purposes of fallout prediction, it is desirable to go beyond the presentation of the experimental data and, if possible, use these data to deduce the mechanisms which govern the uptake of the TeO_2 vapor. If the mechanisms or processes which determine the rate of uptake can be discovered, then it should be possible to extrapolate the experimental data into other regions of temperature and pressure.

There are three basic steps in the uptake of the TeO_2 vapor by the substrate particles and any one of these might be slow enough in comparison with the others to be the rate-determining step. These three steps are: (1) the diffusion of the TeO_2 vapor molecules through the air to

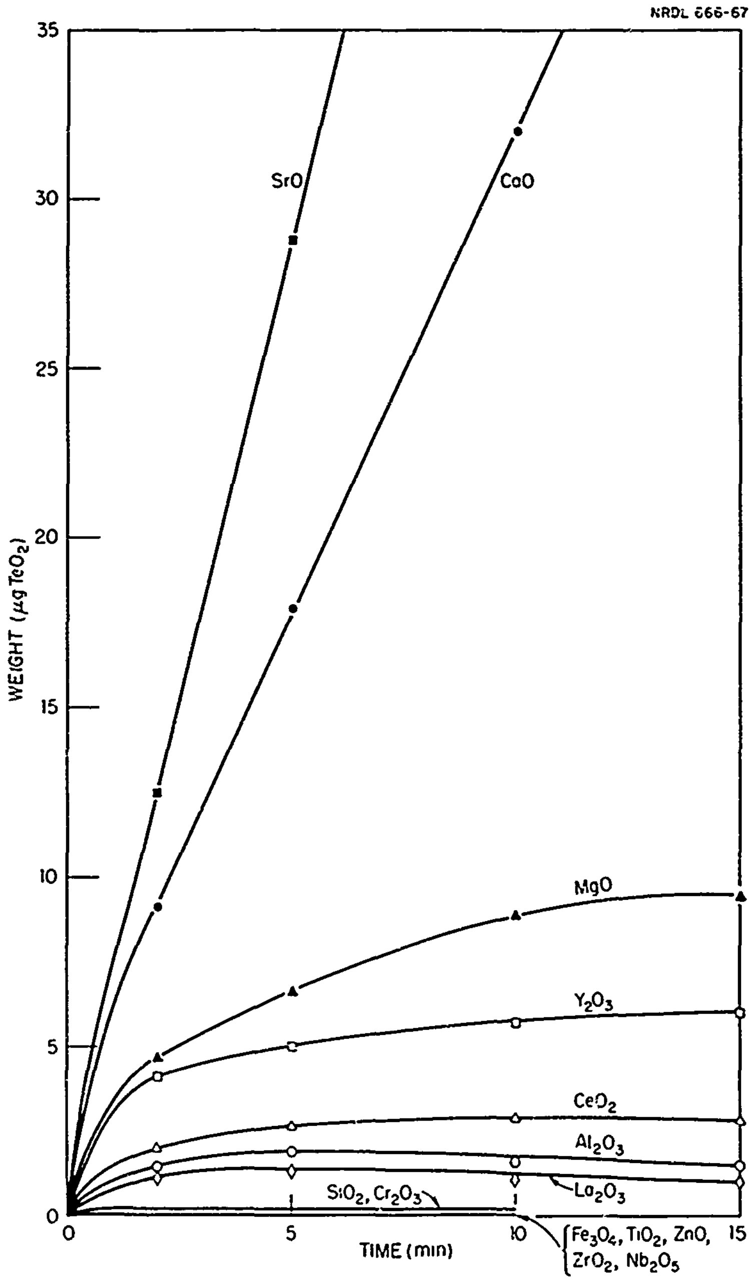

Fig. 10 Uptake of TeO_2 by Solid Oxide Pellets. T = 1400°C, TeO_2 partial pressure = 3.46×10^{-5} atm. The area of the pellets exposed to the TeO_2 vapor was approximately 0.293 cm^2.

the surface of the particle; (2) the reaction and condensation of the TeO_2 vapor molecules at the surface of the particle; and (3) the diffusion of the condensed TeO_2 into the interior of the particle.

If one assumes that the diffusion of the TeO_2 vapor molecules through the air is the rate-determining step, then this process can be described by Maxwell's equation:

$$I = \frac{2\pi d\ D_{12} M\ (P_\infty - P_o)}{RT}$$

where I is the rate of impingement of the vapor species, of molecular weight M, upon a particle of diameter d. D_{12} is the inter-diffusion constant of the vapor species in the gaseous medium. P_∞ is the partial pressure of the vapor at a large distance from the particle and P_o is the partial pressure at the surface of the particle. If vapor diffusion is the rate-determining step, Maxwell's equation shows that, with constant temperature and pressure, the rate of uptake of the TeO_2 vapor will be proportional to the diameter of the particle and therefore that the total amount taken up will be proportional to the product of the particle diameter and time.

If the rate-determining step is the reaction or the condensation of TeO_2 at the surface of the particle, then the rate will be proportional to the surface area of the particle or to the diameter squared. The total amount taken up will be proportional to the product of the diameter squared and time.

If the diffusion of the condensed TeO_2 into the particle is slow compared to the other two steps, and if condensation is reversible, then the outer surface layer of the particle reaches a steady concentration of TeO_2 and further condensation is governed by the rate at which the TeO_2 diffuses away from the surface zone into the particle. As a model for this process one can envisage a spherical particle of the substrate material surrounded by a solution containing the TeO_2 at a constant concentration. A graphical solution of the mathematical relations for this type of diffusion is given by Crank.[3] At early times in the diffusion process,

$$\frac{M_t}{M_\infty} \sim \left[\frac{Dt}{d^2}\right]^{\frac{1}{2}}$$

where $\frac{M_t}{M_\infty}$ is the ratio of the amount of material diffusing into a particle of diameter d at time t to the total amount which diffuses into the particle at infinite time.

D is the diffusion constant of the diffusing material in the particle.

M_∞ is proportional to the volume of the particle, or to d^3, so that, at constant temperature,

$$M_t \sim d^2\, t^{\frac{1}{2}}.$$

Therefore, if diffusion of TeO_2 into the particle is rate-determining, the total amount of TeO_2 taken up will be proportional to the diameter squared of the particle multiplied by the square root of the time. The rate of uptake of TeO_2 will be proportional to the diameter squared divided by the square root of the time.

These relationships are summarized in Table I. It should be emphasized that these relationships are true only for relatively small time intervals during which the composition of the particles does not change appreciably.

Uptake of TeO_2 by Calcium Ferrite Particles as a Function of Particle Size and TeO_2 Partial Pressure

Consider first the uptake of TeO_2 by various-sized calcium ferrite particles at 1400°C as shown in Fig. 2. At this temperature the samples

TABLE I

Rate-Controlling Process	Rate of Uptake of TeO_2 is Proportional to:	Amount of Uptake of TeO_2 is Proportional to:
Diffusion of TeO_2 Vapor Through Air	d	dt
Reaction or Condensation Rate at Surface of the Particle	d^2	d^2t
Diffusion of TeO_2 into Particle	$\frac{d^2}{\sqrt{t}}$	$d^2\sqrt{t}$

take up enough TeO_2 to achieve equilibrium in a few minutes. In order to use Table I as a guide to the elucidation of the rate-determining mechanism, one must use data for early times before an appreciable fraction of the equilibrium uptake has occurred. In Fig. 11 the initial rates of uptake have been plotted as a function of particle diameter and diameter squared. This graph shows that the initial rates are proportional to the diameters of the particles. This indicates that the rate-controlling process is the diffusion of the TeO_2 vapor through the air to the surface of the particles.

If the rate-determining step is the diffusion of the TeO_2 vapor molecules through the air, it should be possible to predict the rate of TeO_2 uptake by the calcium ferrite under varying conditions of temperature and pressure by use of Maxwell's equation. The use of Maxwell's equation requires knowledge of the interdiffusion constant of TeO_2 molecules in air. This inter-diffusion constant is not known but it can be estimated by use of the Stefan-Maxwell equation,

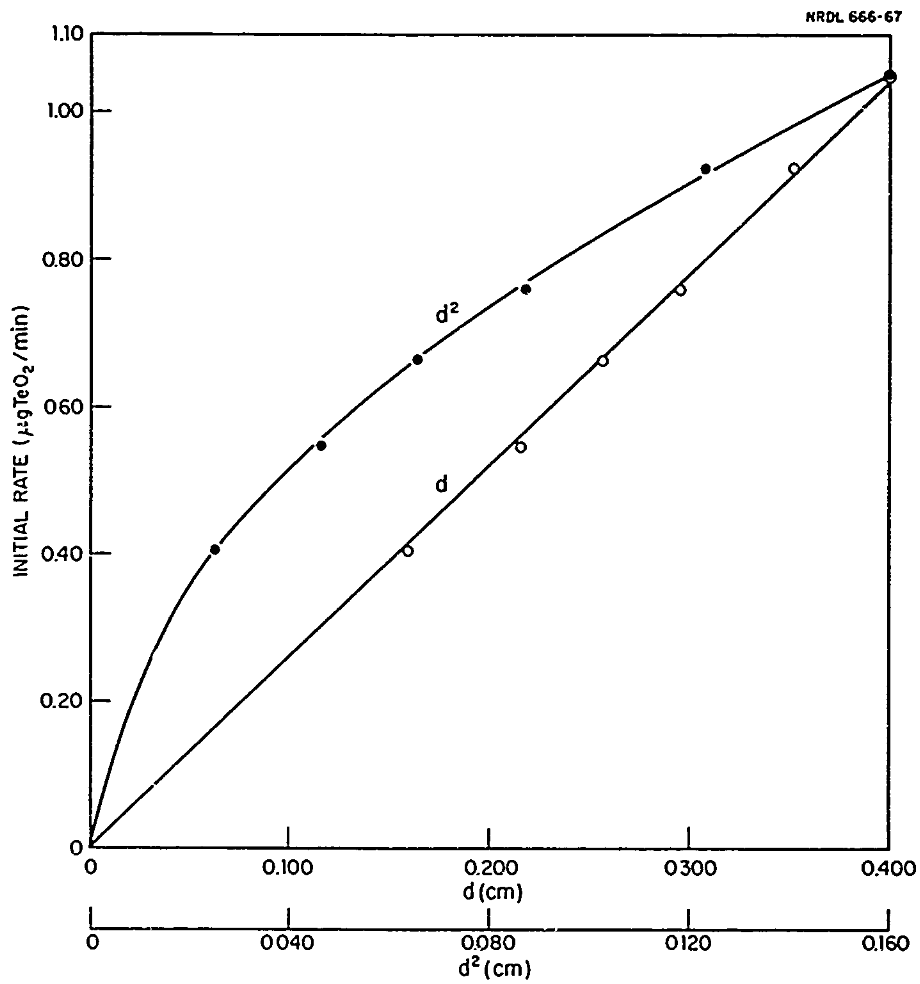

Fig. 11 The Initial Rate of TeO_2 Uptake by Calcium Ferrite Particles Plotted vs. Particle Diameter and vs. Diameter Squared. T = 1400°C, TeO_2 partial pressure = 9.21×10^{-6} atm.

$$D_{12} = \frac{1}{\pi\, \sigma_{12}^2\, (n_1+n_2)} \left[\frac{2kT}{\pi\mu}\right]^{\frac{1}{2}}$$

where σ_{12} is the mean collision diameter of the two vapor species, in this case TeO_2 and air; μ is the reduced molecular mass

$\frac{m_1 m_2}{m_1+m_2}$; and

n_1 and n_2 are the numbers of molecules of each species per cm^3.

The collision diameter of the TeO_2 molecules is not known so it must be estimated. For many common gases, the collision diameter is roughly twice the physical or geometric diameter of the molecule as determined by molecular or atomic radii. From known data on the bond distances of SO_2 and SeO_2 vapor molecules, the average geometric diameter of the TeO_2 molecule was estimated by linear extrapolation and this figure was doubled to give an approximate collision diameter for TeO_2 of 7×10^{-8} cm. By use of this diameter and the known average collision diameter of air, 3.7×10^{-8} cm, the interdiffusion constant of TeO_2 in air was calculated for the range of temperatures and pressures used in this series of experiments.

Maxwell's equation was then used to calculate the mass of TeO_2 molecules which struck and was retained on the surface of the calcium ferrite particles as a function of pressure at 1400°C. Because Maxwell's equation assumes stationary air relative to the particle, it was necessary to apply a small correction factor for the effect of the flow of carrier gas up the furnace tube.[4] This correction amounted to about 14 % and was undoubtedly small compared with the error introduced by uncertainty in the TeO_2 collision diameter.

This calculated rate of TeO_2 condensation on the calcium ferrite particles has been plotted as the dashed line in Fig. 8. It is apparent that the experimentally measured rate is very close to this calculated rate, which agreement indicates that the rate-controlling step is probably the diffusion of the TeO_2 vapor molecules through the air to the surfaces of the particles.

The plot of the calculated uptake rate has a slope of one; that is, the rate is calculated to be directly proportional to the TeO_2 partial pressure. This is because the value of P_o in the quantity $P_\infty - P_o$ in Maxwell's equation has been assumed to be zero. The plot of the experimentally measured rates has a slope of 0.91. This discrepancy may be due to our incorrectly assuming that $P_o = 0$. If, as P_∞ is increased, P_o has a finite value and increases at a greater rate proportionally than P_∞, then the slope of the calculated plot would be less than one.

Also plotted on the same graph is the total uptake concentration of TeO_2 in the calcium ferrite particles at equilibrium. A line with a slope of one has been drawn through these plotted points. This shows that the equilibrium uptake is proportional to the TeO_2 partial pressure; i.e., the system obeys Henry's Law.

Uptake of TeO_2 by Calcium Ferrite Particles as a Function of Temperature

By use of Maxwell's equation the mass of TeO_2 molecules which struck and were retained on the calcium ferrite particles as a function of temperature at a TeO_2 partial pressure of 9.21×10^{-6} atm was also calculated and is shown as the upper dashed line in Fig. 9. The correspondence here between the calculated and experimentally measured rates is not as close as that found for varying pressure.

At low temperatures, from 900 to 1100°C, the experimentally measured rate is close to the calculated rate. There is a pronounced decrease in the rate of uptake just below the melting point of the calcium ferrite.

This drop may be associated with a crystallographic rearrangement of the components in the solid calcium ferrite. The phase diagram for the system $CaO-Fe_2O_3$ shows that (at the composition used in these experiments) between the melting point (1205°C) and 1155°C the two solid phases $CaO{\cdot}Fe_2O_3$ and $CaO{\cdot}2Fe_2O_3$ are both stable.[5] Below 1155°C the $CaO{\cdot}2Fe_2O_3$ disproportionates into $CaO{\cdot}Fe_2O_3$ and Fe_2O_3. It is within this range of temperatures that the uptake of TeO_2 by the calcium ferrite shows unusual features. Not only is there a pronounced drop in the rate of uptake, but the shapes of the graphs of TeO_2 uptake vs. time show peculiar features. Runs made at 1125, 1150, and 1175°C show the uptake of TeO_2 rising to a pronounced maximum within a few minutes of the beginning of the runs and then, as the runs continued, the total uptake of TeO_2 actually decreased. Runs at 1200 and 1100° did not show this maximum.

We felt that this strange behavior might be associated with an unstable or strained condition caused by the rapid cooling of the calcium ferrite from the molten state to room temperature during the formation of the particles on the platinum wire loops. During the course of the run there might be enough molecular rearrangements at the furnace temperature to modify the chemical reactivity of the calcium ferrite.

For a test of this, two pairs of identical calcium ferrite samples were prepared. One sample of each pair was treated in the same manner as were all the previous samples and the other sample of each pair was annealed in air at 1150° for about 1¼ hours before their TeO_2 uptakes were measured. The TeO_2 uptakes were measured on one pair of samples at 1150° and on the other pair at 1100°C. The results are plotted in Fig. 9. The annealing process apparently caused a slight decrease in the rate of TeO_2 uptake at 1100°C. At 1150°C the effect was more pronounced as shown by the fact that there was an appreciable increase in the rate of uptake caused by the annealing process. However, in each case the unannealed new sample was farther away from the old point than it was from the annealed point. Thus, in this region, reproducible behavior is difficult to achieve. However, the effect of annealing is shown also by the fact that the shape of the uptake curve changed markedly. The results for one pair are shown in Fig. 12. The unannealed sample shows a pronounced maximum in the TeO_2 uptake at about 10 minutes, and as the time in the furnace increased to 100 minutes, the amount of TeO_2 in the particle decreased by 82 %. Up to 10 minutes the annealed particle shows about the same TeO_2 uptake as the unannealed particle. After 10 minutes the annealed particle continued to take up TeO_2, but at a slower rate. This result is surprising as it would be expected that the annealing process would result in changing the initial uptake as compared with the unannealed sample and that after a long time in the furnace both samples would adjust to the furnace temperature and would reach the same equilibrium uptake. Actually, just the opposite of this process occurred. No explanation of this behavior has been discovered and the problem was not pursued further.

As an additional check on the rate-determining mechanism at low temperatures, two series of runs with varying particle sizes were made, the first at 1200°C and the second at 1000°C. The runs at 1200°C showed so much variation in the initial uptake rates that no systematic trend was observed as a function of particle size and deductions about the nature of the rate-determining step were not possible. At this temperature the TeO_2 uptake for each particle size reached an apparent equilibrium value after about 40-70 minutes in the furnace (Fig. 3). These equilibrium uptakes were linear functions of the squares of the particle diameters, which fact indicates that the apparent equilibrium was due to a surface saturation. This was confirmed by exposure of a calcium ferrite particle to TeO_2 vapors at 1200°C for 80 minutes and then embedding of the particle in plastic and grinding away of the plastic to expose a semi-section of the particle. A radioautograph of this semi-section showed that all the radioactive TeO_2 was confined to a surface zone on the particle.

For the particles exposed at 1000°C, a plot of initial rate of TeO_2 uptake vs. particle diameter was linear. This confirms the supposition

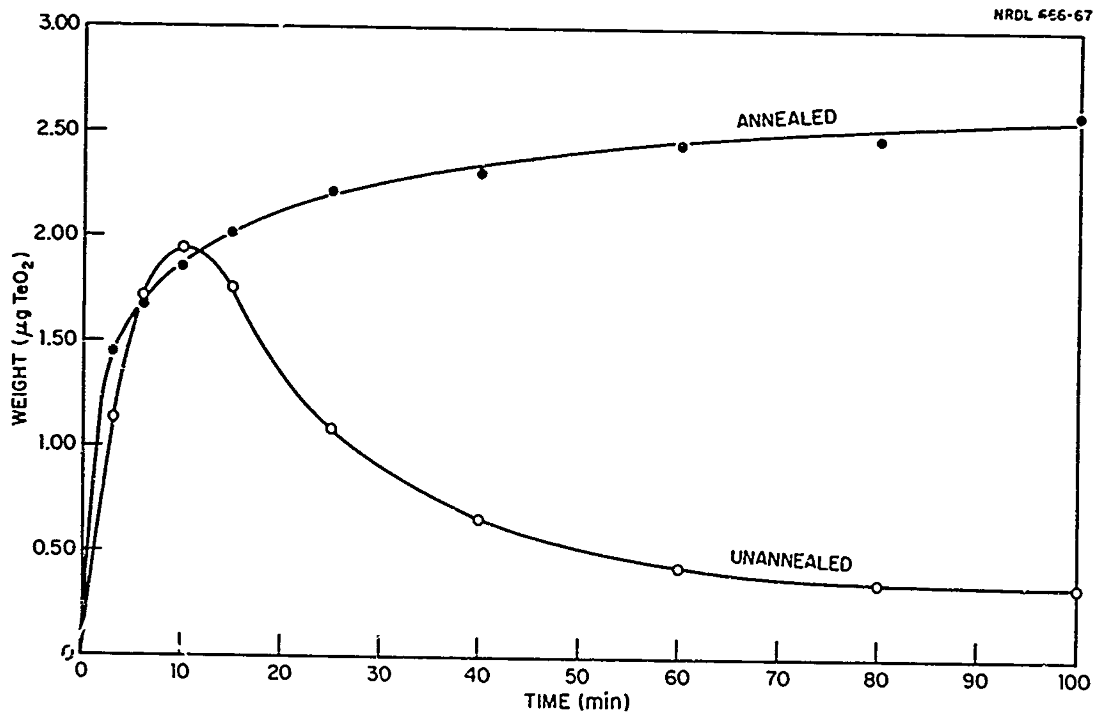

Fig. 12 Uptake of TeO_2 by an Annealed and an Unannealed Particle of Calcium Ferrite. The annealed particle was heated in air at 1150°C for 1-1/2 hours before the measurement of the uptake of TeO_2. T = 1150°C, TeO_2 partial pressure = 9.21×10^{-6} atm.

that the rate controlling process at these low temperatures is the diffusion of the TeO_2 molecules through the air, as it is at $1400^{\circ}C$.

For temperatures above the melting point, from 1250 to $1500^{\circ}C$, the initial uptake rate is close to the calculated rate but decreases with increasing temperature. Possibly this decrease is caused by a decrease in the reactivity or solubility of the TeO_2 in the melt and, because of increased re-evaporation and rate of diffusion, at higher temperatures the rate of surface reaction may become increasingly important as the rate-determining process.

The fact that, except near the melting point, the rate-controlling step for the uptake of TeO_2 vapor by the calcium ferrite is diffusion of the TeO_2 through the air implies a rapid rate of surface reaction and rapid diffusion, or mixing, of the condensed TeO_2 into the calcium ferrite particles. For a check of this, three samples of calcium ferrite were prepared. The samples were exposed separately to TeO_2 vapor at $1400^{\circ}C$, one for 2 minutes, one for 8 minutes, and one for 20 minutes. These times were chosen because calcium ferrite samples of these sizes reach about 50 % of their equilibrium uptake in about 2 minutes and reach equilibrium in about 8 minutes. The particles were then embedded in plastic, the plastic was ground away to expose semi-sections of the particles, and radioautographs were made.

The radioautographs of the particles exposed to the TeO_2 vapor for 8 and for 20 minutes showed the radioactivity evenly distributed throughout the volumes of both of the particles which indicates that true equilibrium was achieved by about 8 minutes. The radioautograph of the particle exposed for 2 minutes (about 50 % uptake) showed the radioactivity distributed somewhat irregularly throughout the particle with higher concentrations toward the surface and around the platinum wires. It appears as if mixing was aided by convection as well as by rapid diffusion. The calcium ferrite melts are quite fluid at $1400^{\circ}C$ and it is likely that convection played a part in the rapid uptake of the TeO_2. The high TeO_2 concentrations around the platinum wires suggest that heat conduction along the wires helped establish convection currents near the wires. By contrast a radioautograph of a clay loam particle exposed for 2 hours at 1400°C* showed that all the radioactivity was confined to a zone near the surface of the particle.

From the data on the equilibrium uptake of TeO_2 at the various temperatures above the melting point of calcium ferrite, it is possible to calculate the differential heat of solution of TeO_2 in the calcium ferrite melt. The equation,

$$\left[\frac{\partial \ln N_2}{\partial T}\right]_P = \frac{\bar{H}_2 - H_2'}{RT^2},$$

is used, in which N_2 is the solubility of the TeO_2 in the calcium ferrite melt at temperature T at constant pressure,

$\bar{H}_2$ is the partial molar heat content of TeO_2 in a saturated solution of calcium ferrite,

H_2' is the molar heat content of pure TeO_2 vapor.

$\bar{H}_2 - H_2'$ was calculated from the slope of the graph of $\log_{10} N_2$ vs. $\frac{1}{T}$ (see Fig. 13) and was found to be -64.2 Kcal/mole.

Uptake of TeO_2 by Clay Loam Particles

The data on the uptake of TeO_2 by the various sizes of clay loam particles at constant pressure and temperature do not afford a means of determining the rate-controlling mechanism. Figures 5, 6 and 7 show that the measured initial rates of TeO_2 uptake by the various size particles are highly irregular and do not vary in a systematic fashion with particle diameter. In general, the larger the particle the greater the average rate of TeO_2 uptake, but the magnitude of the uptake is so small

*At 1400°C, clay loam is within its broad melting region, but is viscous rather than fluid.

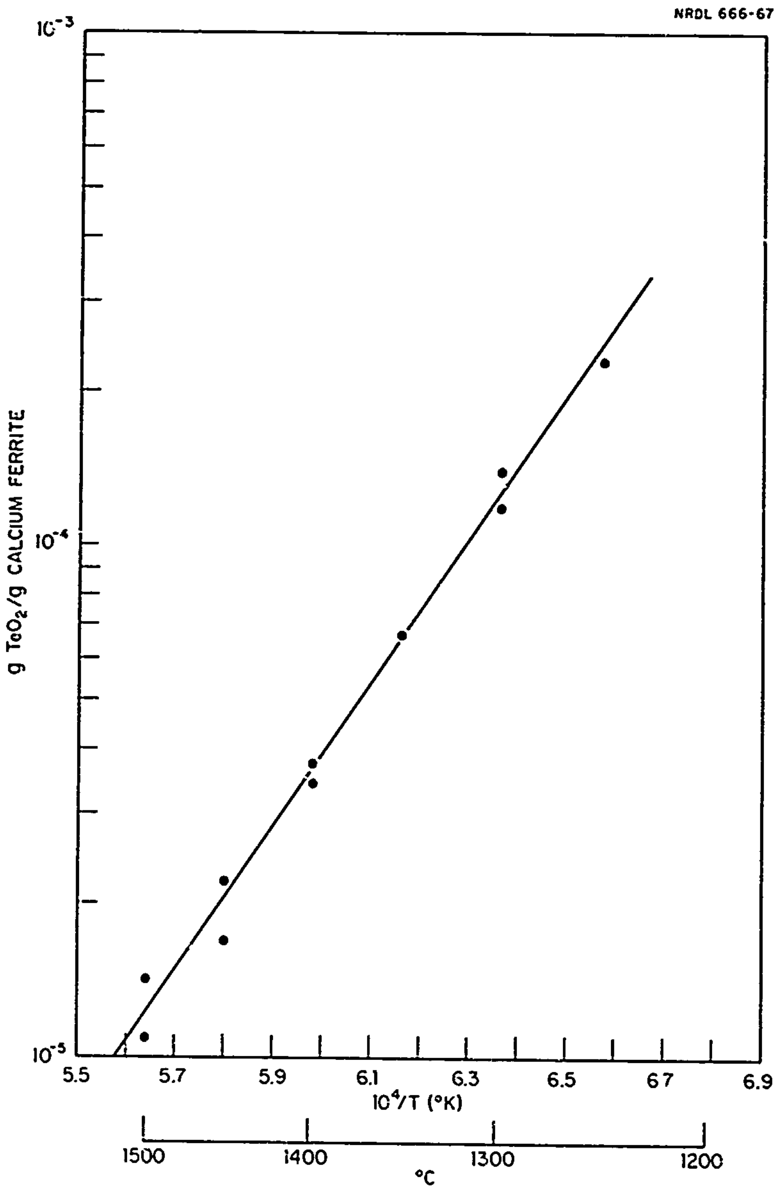

Fig. 13 The Equilibrium-Uptake Concentration or Solubility, of TeO_2 Vapor in Calcium Ferrite as a Function of Temperature. TeO_2 partial pressure = 9.21×10^{-6} atm.

that apparently differences in sample surface characteristics or other experimental conditions introduce large variabilities in the rates of uptake. The data on the initial rate of TeO_2 uptake with varying pressure and temperature (Figs. 8 and 9) also show considerable variability, but it is apparent diffusion of TeO_2 vapor molecules through the air is not the rate-determining process. The initial rate is 2 to 3 orders of magnitude lower than that calculated with Maxwell's equation.

This leaves the possibility that the TeO_2 uptake rate is determined by the rate of surface reaction, the rate of diffusion of the condensed TeO_2 within the particles, or a combination of both processes. One could check the possibility that the simple diffusion model describes the rate process if one knew the diffusion constant and the equilibrium uptake of the TeO_2 in the clay loam. No data on the diffusion of TeO_2 in the clay loam melt are available. However, Norman et al.[6] have measured the diffusion constant of TeO_2 in a calcium aluminum silicate melt of the following composition:

CaO	23.3 wgt. %
Al_2O_3	14.7 wgt. %
SiO_2	62.0 wgt. %

For a check of the possibility that diffusion of the TeO_2 in the particle is the rate-controlling process, two samples were prepared: one of clay loam with a particle diameter of 0.282 cm and one of the calcium aluminum silicate (CAS) with a diameter of 0.277 cm. These two samples were exposed separately in the furnace at 1410°C to a TeO_2 partial pressure of 1.14×10^{-5} atm. The samples were removed from the furnace periodically and counted and then returned to the furnace. This process was kept up until the samples reached equilibrium. This took about 50 hours for the clay loam and about 70 hours for the CAS. The final equilibrium uptakes were 3.7×10^{-5} gms TeO_2/gm clay soil and 1.8×10^{-5} gms TeO_2/gm CAS (Norman et al. report a TeO_2 equilibrium uptake in CAS of approximately 1.4 x 10^{-5} gms TeO_2/gm CAS at 1260°C and at a TeO_2 partial pressure of 1.14 x 10^{-5}).

These data and Norman's value of 1.07 x 10^{-6} cm^2/sec for the diffusion constant of TeO_2 in CAS at 1410°C were used in the relation given by Crank[3] to calculate the uptake of TeO_2 by each of the two samples. In Fig. 14, curves showing the experimentally measured uptake of TeO_2 at early times are plotted for both the clay loam and the CAS samples. Also plotted are the TeO_2 uptake curves calculated by use of Crank's relationship. It can be seen that the rates of TeO_2 uptake predicted by the calculations based on the simple diffusion model are considerably larger than the experimentally measured uptakes for both the clay loam and the CAS.

It is apparent that neither diffusion of the TeO_2 vapor molecules through the air nor diffusion of the TeO_2 in the interior of the particles is the rate-determining process. If the rate of TeO_2 reaction at the surface of the particles were rate-determining, then the rate of uptake, during an initial period which is short compared with the time to reach equilibrium, should be independent of time. The rate of TeO_2 uptake on the clay loam particles actually decreases markedly with time, indicating that the rate of surface reaction is not the rate-controlling step. It seems that the uptake mechanism cannot be described adequately by a single rate-determining process.

An attempt was made to fit the two long-time equilibrium uptake curves to the general rate equation. It was found that the uptake by the clay loam sample approximated a 1.0 order process and the uptake by the CAS a 1.3 order process. However, the correspondence between the curves calculated by use of the general rate equation and the experimentally measured curves was not good and there was a marked deviation in the uptake rates at early times.

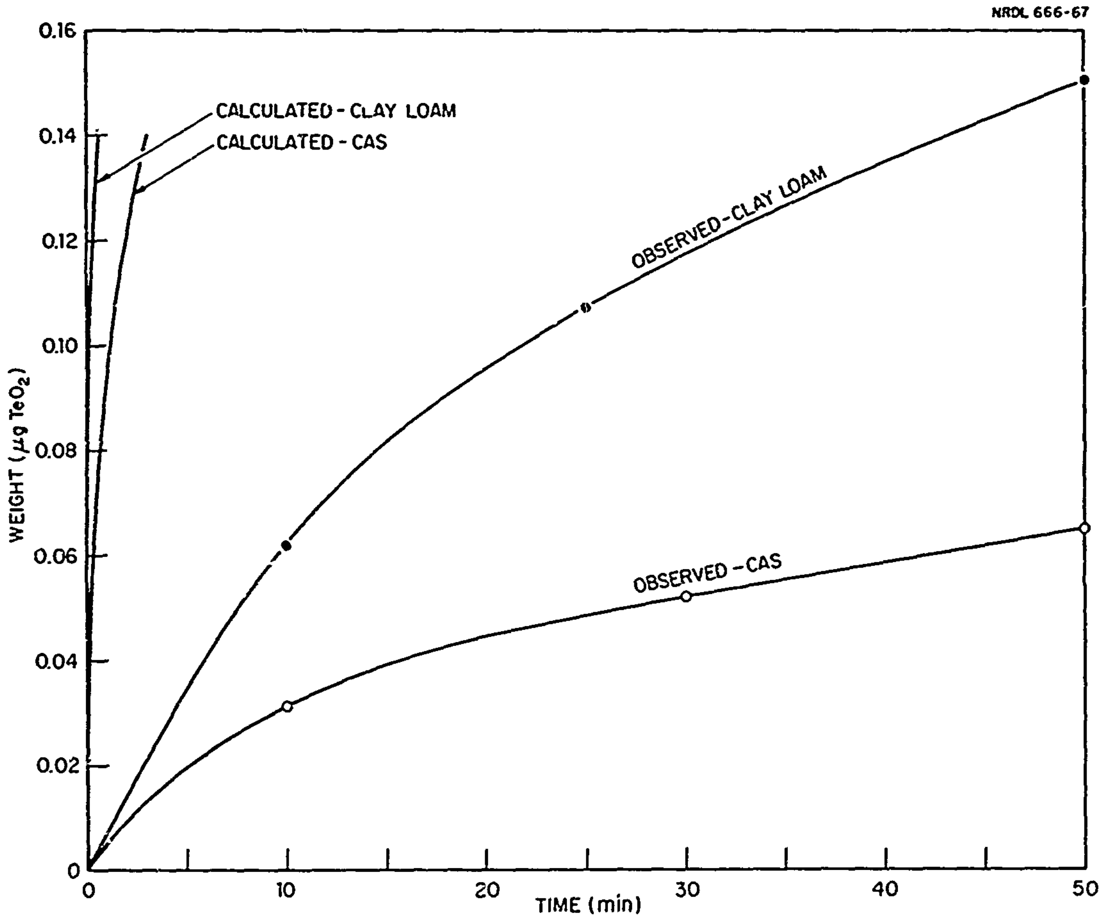

Fig. 14 Uptake of TeO_2 by a Particle of Clay Loam 0.282 cm in Diameter and by a Particle of Calcium Aluminum Silicate 0.277 cm in Diameter. The calculated uptake curves were obtained by use of the simple diffusion model and a diffusion constant for TeO_2 of 1.07×10^{-6} cm^2/sec. T = 1400°C, TeO_2 partial pressure = 1.14×10^{-5} atm.

In many of the clay loam samples it was observed that the uptake of TeO_2 increased steadily for a few minutes until an amount on the order of a monolayer had condensed and then the uptake rate decreased appreciably. All the evidence seems to indicate that the mechanism which governs the uptake rate may change during the course of the reaction and that no single relationship can be used to describe the entire process. Probably, the rate is determined both by a slow surface reaction in which the sticking coefficient of the TeO_2 vapor molecules is considerably less than one and by a slow diffusion rate of the condensed TeO_2 in the particles.

Uptake of TeO_2 by Solid Oxide Samples

When TeO_2 vapor is taken up by the various substrate materials, it is not clear which of the components of the melts is reacting with the TeO_2. For obtaining a qualitative notion of the relative degree of reactivity of the TeO_2 with the different components of the melts, the uptake of TeO_2 by a series of 14 simple solid oxides at 1400°C was measured (Fig. 10). The oxides studied fell into three groups with reference to their tendency to react with TeO_2. Fe_3O_4,* TiO_2, ZnO, ZrO_2 and Nb_2O_5 take up a very small quantity of TeO_2, probably amounting to no more than a part of a monolayer, and SiO_2 and Cr_2O_3 take up very little more. La_2O_3, Al_2O_3, CeO_2, Y_2O_3 and MgO take up an intermediate amount of TeO_2 and SrO and CaO take up large amounts. In general, the more basic the oxide the greater its reactivity with TeO_2. An exception seems to be ZnO. However, these results are only qualitative since some of the samples tended to crumble or shrink in the furnace so that there were irregularities in the surface areas exposed. Also, the rates of TeO_2 reaction will be affected by the rates of diffusion of the TeO_2 in the solid oxides and the particle size and microscopic surface structure of the oxide powders.

*Fe_2O_3 converts to Fe_3O_4 under the conditions of the experiment.

Influence of the Composition of the Calcium Ferrite Substrate on the TeO_2 Uptake

These results suggest that in complex melts, such as the clay loam and calcium ferrite, the uptake of TeO_2 is due predominantly to its reactivity with CaO and MgO (and probably Na_2O and K_2O) rather than with the more acidic oxides such as SiO_2 or Fe_2O_3. For a test of this, a series of four calcium ferrite samples were prepared with varying concentrations of CaO (15, 20, 24 and 28 wgt. % CaO). The uptake of TeO_2 vapor at a partial pressure of 1.05×10^{-5} atm and at a temperature of $1410^{\circ}C$ was measured on particles 0.240 cm in diameter at each of the four compositions. The results are shown in Fig. 15.

Changing concentrations of CaO in the melt seem to have little effect on the initial rate of TeO_2 uptake except for the unexplained increase in the rate by the sample with the highest CaO concentration. If the rate were determined only by the rate of diffusion of the TeO_2 vapor through the air, then changing the particle compositions would not have an effect on the initial rate.

The equilibrium uptake of TeO_2 by each sample has also been plotted and in this case there is a marked increase in the total TeO_2 uptake as the CaO concentration is increased.

The measurements of the TeO_2 uptake by the solid oxide samples show that the degree of reactivity of the TeO_2 with the Fe_2O_3 is almost negligible compared with its reactivity with CaO. If this is true, then the uptake of TeO_2 by the calcium ferrite should be due only to the reaction of the TeO_2 and CaO and, where the uptake of TeO_2 is so small that the composition of the melt is not changed appreciably, the amount of TeO_2 taken up should be proportional to the activity of the CaO in the melt.

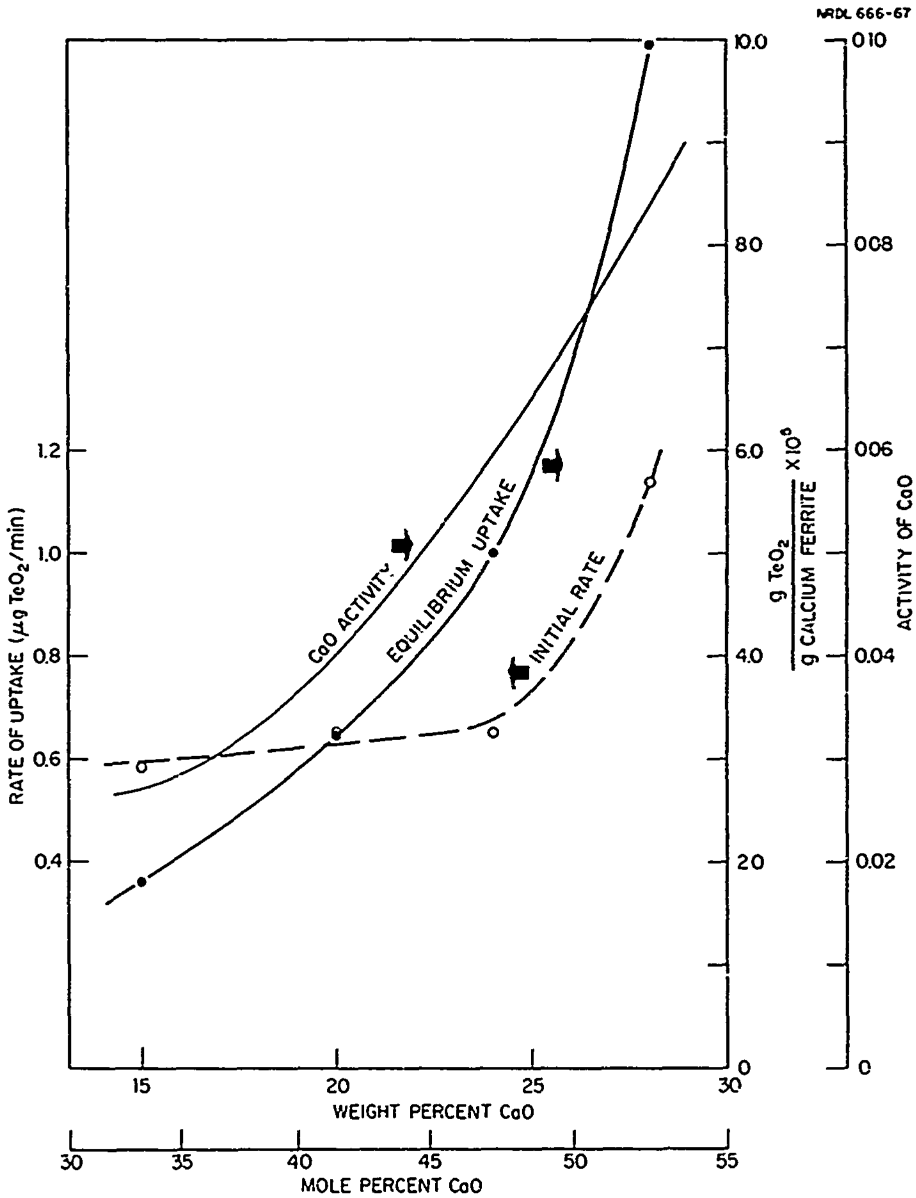

Fig. 15 The Rate of Uptake and the Equilibrium Concentration of TeO_2 by the Calcium Ferrite as a Function of Particle Composition. T = 1410°C, TeO_2 partial pressure = 1.05×10^{-5} atm. The activity of CaO (relative to pure solid CaO at 1550°C) is shown.

Turkdogan[7] has calculated the activity of CaO in the melts of the ternary system CaO-FeO-Fe_2O_3 at 1550°C. In order to use Turkdogan's calculations it is necessary to know the composition of the calcium ferrite samples in terms of the ternary system. Phillips and Muan[8] have measured the composition of calcium ferrite melts at the liquidus in air and their data can be used to determine the approximate composition of the calcium ferrite used here at 1410°C. Actually the amount of FeO in CaO-rich ferrite melts is not great. The ferrite melt containing 15 wgt. % CaO has about 5 wgt. % FeO and 80 wgt. % Fe_2O_3 at 1325°C and the melt containing 28 wgt. % CaO has about 1 wgt. % FeO and 71 wgt. % Fe_2O_3 at 1310°C.

With the use of the data of Phillips and Muan and of Turkdogan, the approximate activity of CaO in the calcium ferrite samples was calculated and has been plotted in Fig. 15. While the CaO activity data is not accurate, nevertheless there is a correspondence between the equilibrium uptake of TeO_2 and the activity of the CaO in the melts. This suggests the possibility of determining relative activities of one component of a melt at high temperatures by measuring the uptake of radioactive vapor. The restrictions are that the radioactive vapor react with only one component of the melt and that the amount of vapor taken up does not change the composition of the melt appreciably.

Influence of Humidity on the TeO_2 Uptake

As it is known that TeO_2 can form a hydrated vapor molecule $TeO(OH)_2$,[9] two series of measurements were made at 1410°C to determine the effect of water vapor on the uptake of TeO_2. The first series of measurements was done with dry air as the carrier gas and the uptake of TeO_2 on calcium ferrite and clay loam samples was measured. The second series was done under identical conditions except that the incoming air was essentially saturated with water vapor at 28°C. A small increase (about 10 %) was observed in the rate of vaporization of the

TeO_2 source, but there was no detectable difference in the rate of TeO_2 uptake between the dry and wet air condition by either the calcium ferrite or clay loam.

Comparison of the Uptake Behavior of TeO_2 Vapor with that of MoO_3 Vapor

It is interesting to compare qualitatively the results of these measurements of the uptake of TeO_2 vapor with that of MoO_3 vapor[1] on the same sample materials and over similar ranges of temperature and pressure. In general, the reactivity of the MoO_3 was much greater than that of the TeO_2 with both the calcium ferrite and the clay loam. At about 1400°C and at comparable pressures the equilibrium uptake of MoO_3 was approximately 10^4 times that of the TeO_2 in the case of calcium ferrite and approximately 10^3 times that of the TeO_2 in the case of clay loam samples.

These large differences in equilibrium uptake were not reflected in similar large differences in the initial rates of uptake. In spite of the factor of 10^4 in the ratio of the final uptakes, the initial rate of uptake of the MoO_3 and of the TeO_2 by the calcium ferrite at 1400°C was the same to within a factor of about two to three. This is because the rate-determining step in both cases is the diffusion of the vapor molecules through the air to the surfaces of the particles and the diffusion rates of the MoO_3 and TeO_2 vapor molecules are roughly comparable. The greater reactivity of the MoO_3 with the calcium ferrite results in a situation in which the initial rate of uptake continues with little change over comparatively long times. On the other hand, the low reactivity of the TeO_2 results in a situation in which the uptake rate decreases rapidly from its initial rate and reaches zero when equilibrium is achieved within a few minutes.

On the other hand, in the case of the clay loam there was a substantially greater rate of uptake of the MoO_3 than of the TeO_2. It is difficult to make a direct comparison of the ratios of the initial uptake rates, primarily because of the poor quality of the TeO_2 uptake data. But if estimates are made of the uptakes at 1400°C on the clay loam under comparable conditions of pressure and particle size, then the initial rate of MoO_3 uptake is roughly 10^2 times the initial rate of TeO_2 uptake, and as mentioned earlier the MoO_3 equilibrium uptake is about 10^3 times the TeO_2 equilibrium uptake.

No single, simple mechanism was discovered for the rate-determining process for the uptake of either MoO_3 or TeO_2 by the clay loam. For both oxides the rate of uptake seemed to be determined by a combination of both a slow surface reaction and slow diffusion of the condensed species within the particles.

Both MoO_3 and TeO_2 formed stable hydrated oxide vapor molecules when humid air was used instead of dry air as the carrier gas. Enhanced evaporation of the source material was observed for both oxides but there was no important change in the rates of uptake in either case.

CONCLUSION

Caution must be used in the application of the data of this report to actual fallout formation processes. It must be borne in mind that under the conditions existing in a nuclear fireball the temperature and pressure are not only changing rapidly with time but are variable from one part of the fireball to another. Also the radioelements themselves constitute only a very small fraction of the total vaporized material and may form complex vapor species with the inert vapor atoms or molecules. These complex vapor molecules may have appreciably different rates of uptake than the simple molecules studied here. In view of these major uncertainties, the experimental variations and errors in the measured rates of uptake reported here are probably not important.

On the other hand, in spite of these inherent difficulties in the application of the data to the actual nuclear situation, major insights into the mechanisms governing the formation processes of radioactive fallout particles have been achieved. The rates of uptake by calcium ferrite of MoO_3 and TeO_2 vapor (and probably many other vapor species as well) can be quite adequately predicted over large ranges of temperature and pressure by kinetic theory alone without recourse to physical-chemical parameters such as solubility or diffusion rates within the liquid or solid substrate materials. This same mechanism can probably be used to predict the rate of uptake of the more refractory oxide vapors by silicate substrates.

The poor reproducibility exhibited by the clay loam is probably not of operational concern in view of the small affinity of the loam for the TeO_2 vapor under the conditions studied. The annealing effect observed for calcium ferrite will probably be small also because the range of temperature involved is small and there will be a correspondingly small time the system will spend in this region of behavior.

Two approaches are being used to extend the usefulness of the information contained in this and in the first report of this series.[1]

First, measurements will be made of the rate of uptake of rubidium oxide vapor by substrates of calcium ferrite and clay loam. Rubidium oxide is quite different chemically from either MoO_3 or TeO_2, and this study should elucidate the uptake behavior of the more basic oxides.

Second, a mathematical model is being developed which, it is hoped, can be used to calculate the rates of uptake of such vapors as MoO_3 and TeO_2 by silicate substrates. This is a somewhat complicated problem involving as it does the interdependent variables of a slow surface reaction and a slow rate of diffusion of the condensed material within the substrate particles. If successful, this formulation can be used to predict the rates of uptake of various oxide vapors by silicate substrates beyond the ranges of temperatures and pressures covered in this series of measurements.

The fact that there were significant differences in the rates and mechanisms of uptake of the MoO_3 and TeO_2 vapor between the calcium ferrite and the silicate substrates emphasizes the need for caution when applying theories derived from measurements of fallout formed from one kind of soil to fallout formed from another kind of soil.

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13. ABSTRACT

In a program for elucidation of the process of formation of radioactive fall-out, ~~we measured~~ the rates at which substrate samples of calcium ferrite and of clay loam took up vaporized TeO_2. The rate measurements were made for uptake in air from 900 to 1500°C and over a TeO_2 partial-pressure range of about ~~5 x~~ 10^{-7} to ~~2 x~~ 10^{-4} atm. ~~We~~ found that the rate of uptake of TeO_2 by the calcium ferrite was two to three orders of magnitude faster than the rate of uptake by the clay loam. The rate-controlling process for the uptake of TeO_2 vapor by the calcium ferrite was the diffusion of the TeO_2 vapor molecules through the air. No unique rate-controlling process was found for the uptake of TeO_2 vapor by the clay loam. In this system, the rate seemed to be controlled both by a slow rate of reaction of the TeO_2 at the clay loam surface and by the slow diffusion of the condensed TeO_2 into the clay loam.

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